

Effect of barium chloride on nucleation, growth and properties of L-alanine single crystals

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Abstract

Solubility and nucleation studies were carried out for the samples of undoped and barium chloride doped L-alanine. Single crystals of the samples were grown from aqueous solution by slow evaporation method. Structure of the grown crystal was found to be orthorhombic by X-ray diffraction technique and UV-visible-NIR transmittance spectra were recorded for the samples to analyze the transparency in visible and near infrared region (NIR). Linear optical constants such as absorption coefficient, reflectance and refractive index for the samples have been evaluated. Microhardness studies were carried out to check the mechanical strength of the grown crystals and it is found that barium chloride doped L-alanine crystals are more harder than the undoped L-alanine crystal. Frequency and temperature dependence of dielectric constant and loss factor of the samples analyzed and SHG studies for the samples were carried out to understand the NLO activity.

Keywords: Crystal growth; nucleation; doping; L-alanine; NLO; microhardness; optical parameters; SHG; dielectric parameters

1. Introduction

Most of the amino acids and their complexes are the interesting nonlinear optical (NLO) materials and they have potential applications in Second Harmonic Generation (SHG), optical storage, optical communication, photonics etc. Nonlinear optical (NLO) materials with large second order optical nonlinearities have received much importance for better second harmonic conversion efficiency [1-4]. Special interest on amino acid based materials is attributed to their good nonlinearity, high laser damage threshold, low UV cut-off wavelength and moderate thermal and mechanical properties. L-alanine can be considered as the fundamental building block of more complex inorganic acids which shows strong nonlinear behavior and many researchers showered their interest to find organic and inorganic complexes of L-alanine crystals with better SHG efficiency [5-7]. L-alanine is an organic NLO crystal that contains an acid functional group and an amine functional group on adjacent carbon atoms. If both the amino and carboxyl groups are attached to the same carbon atom, it is called as α -amino acid and L-alanine is an α -amino acid. The second harmonic generation (SHG) efficiency of L-alanine is about one third of that of KDP crystal [8-12]. In the present work, single crystals of undoped and barium chloride doped L-alanine were grown by solution method with slow evaporation technique. The grown crystals were subjected to various characterization studies such as solubility, nucleation kinetic studies, X-ray diffraction studies, UV-visible spectral studies, hardness studies, dielectric studies and SHG studies.

2. Experimental procedure

2.1 Solubility and growth

L-alanine and barium chloride salts were purchased commercially and used for the synthesis of the barium chloride doped L-alanine samples. To obtain barium chloride doped samples, 1, 3 and 5 mole % of barium chloride was added to the solutions of L-alanine separately and it was heated at 60° C and stirred well till the doped samples were obtained.

Here let the samples be called as LABC1, LABC3 and LABC5 for L-alanine doped with 1 mole% of barium chloride, L-alanine doped with 3 mole% of barium chloride, L-alanine doped with 5 mole% of barium chloride respectively. Solubility of the samples was measured at different temperatures by gravimetric method. Variations of solubility with temperatures are shown in Figure 1. It is observed from the results that the solubility increases with temperature for the samples and it is found to be more for barium chloride added L-alanine samples. It is clear that for the doped samples, the solvent is able to accommodate an increased amount of solute for the saturation at the same temperature. The increase in solubility for the barium chloride doped samples may lead to change of thermodynamic parameters such as surface concentration of growth species and the surface energy and hence it may be responsible for the change in the solubility and other growth parameters [13,14]. In accordance with the solubility data, the calculated amount of reactants were dissolved in double distilled water and stirred well for 2 hours to ensure uniform concentration through the entire volume of the solution. Under room temperature the solution was allowed to take crystallization process by slow evaporation technique. After 25 days the transparent and colourless crystals were harvested.

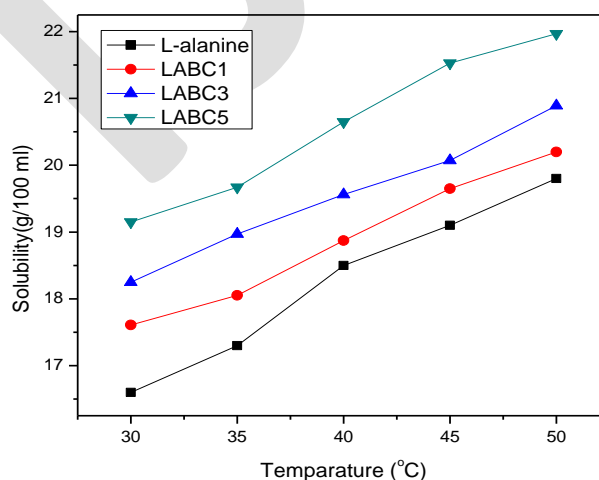


Fig.1: Solubility curves for pure and barium chloride doped L-alanine samples

2.2 Nucleation kinetic studies

Nucleation is the precursor and the most important phenomenon for crystal growth. Once the nucleation occurs in the supersaturated solution, the nucleus grows quickly and a bright sparkling particle is seen. The time interval between the creation of supersaturation and the formation of critical nuclei is called as the induction period and it is influenced by supersaturation, type of solvent, purity of the sample, temperature, pH value of the solution etc. To calculate the nucleation parameters, induction period is necessary and the experiment for measuring induction period for the samples was performed at selected degrees of supersaturation (S), viz. 1.1, 1.15, 1.2, 1.25 at room temperature (30 °C) by isothermal method [15]. From the measured values of induction period, the critical nucleation parameters such as radius of critical nucleus (r^*), Gibbs free energy change (ΔG^*), number of molecules in the critical nucleus (n) and nucleation rate (J) were determined and the obtained results are presented in the table 1. It is observed from the results that the critical nucleation parameters such as radius of critical nucleus, Gibbs free energy change and number of molecules (n) in the critical nucleus decrease with supersaturation ratio (S) and these parameters increase when concentration of barium chloride in the solution is increased. The supersaturation and presence of impurities in the solution have an important role in controlling the nucleation rate and nucleation parameters during the growth of crystals. Studies on nucleation kinetics of crystalline samples are carried out in order to have the controlled nucleation rate. The number of crystals produced in the supersaturated solution is expressed as nucleation rate (J) and the values of J increase as the supersaturation ratio and doping concentration increase.

Table 1: Summary of critical nucleation parameters for pure and urea doped L-alanine samples

Sample	S	$\Delta G^* \times 10^{-20}$ (joules)	$J \times 10^{24}$ nuclei/s/volume	$r^* \times 10^{-9} \text{ m}$	n
Pure L-alanine	1.1	7.640	2.160	0.991	38
	1.15	3.551	3.376	0.675	11
	1.2	2.082	5.566	0.584	5
	1.25	1.394	6.433	0.476	2
LABC1	1.1	7.851	3.453	1.002	40
	1.15	3.652	4.416	0.695	13
	1.2	2.146	6.437	0.594	7
	1.25	1.432	7.897	0.489	4
LABC3	1.1	8.004	5.456	1.045	43
	1.15	3.722	7.032	0.703	15
	1.2	2.218	7.354	0.634	8
	1.25	1.542	8.865	0.502	5
LABC5	1.1	8.893	7.345	1.124	45
	1.15	4.138	7.845	0.784	17
	1.2	2.456	9.877	0.685	11
	1.25	1.645	9.945	0.523	7

2.3 Instrumentation details

The grown crystals were subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK_α ($\lambda = 0.71069 \text{ \AA}$) radiation to evaluate the lattice parameter values. To confirm the nonlinear optical property, Kurtz and Perry powder SHG test was carried out for the grown crystal using Nd:YAG Q-switched laser which emits the first harmonic output of 1064 nm. Microhardness measurement was carried out using a LEITZ microhardness tester, fitted with a Vickers diamond pyramidal indenter. The well polished crystal was placed on the platform of Vickers microhardness tester and the

loads of different magnitudes were applied in a fixed interval of time of 10 seconds. UV-visible transmittance spectra for the grown crystals were recorded in the region 190-1100 nm using a Varian Cary 5E UV-Vis-NIR spectrophotometer and using the values of transmittance reflectance, absorption coefficient and refractive index were evaluated. The dielectric constant and dielectric loss factor ($\tan \delta$) measurements were carried out to an accuracy of $\pm 2\%$ using LCR meter (Agilent 4284A) with different frequencies at various temperatures.

3. Results and discussions

3.1 Structural analysis

Single crystal X-ray diffraction analysis was carried out using a Bruker AXS diffractometer with $\text{MoK}\alpha$ ($\lambda = 0.7170 \text{ \AA}$) radiation to identify the lattice constants. The single crystal X-ray diffraction studies confirm the orthorhombic structure of the grown crystals. The lattice parameters of the samples are provided in the table 2. Here the angular lattice parameters for all the samples are observed to be 90° . Structure of grown crystal was not changed when barium chloride was introduced into L-alanine as the dopant but due to incorporation of the dopant, there is slight changes in lattice constants of samples.

Table 2: The axial parameters and volume of unit cell for the undoped and barium chloride crystals

Samples	Unit Cell Parameters	Volume of unit cell
Undoped L-alanine	$a=5.769 \text{ \AA}$ $b=6.037 \text{ \AA}$ $c=12.338 \text{ \AA}$	$V=429.75 \text{ \AA}^3$
LABC1	$a=5.717 \text{ \AA}$ $b=6.034 \text{ \AA}$ $c=12.337 \text{ \AA}$	$V=430.60 \text{ \AA}^3$
LABC3	$a=5.754 \text{ \AA}$ $b=6.048 \text{ \AA}$ $c=12.398 \text{ \AA}$	$V=434.43 \text{ \AA}^3$
LABC5	$a=5.915 \text{ \AA}$ $b=5.959 \text{ \AA}$ $c=12.444 \text{ \AA}$	$V=438.67 \text{ \AA}^3$

3.2 Linear optical studies

Transmission range and transparency cut-off are very important parameters, especially for crystals used in SHG. Transmittance values of the grown crystals are given in the figure 2. The crystal has excellent transmission in the entire visible region. The lower-cut off wavelength is around 240 nm. The good transmission of the crystal in the entire visible region suggests its suitability for second harmonic generation devices. From the results, it is noticed that the transparency gets increased when barium chloride is added as dopant into L-alanine crystals. The optical absorption coefficient (α) was calculated from transmittance using the following relation

$$\alpha = \frac{1}{d} \log \left(\frac{1}{T} \right)$$

where T is the transmittance and d is the thickness of the crystal. The reflectance (R) was determined using the following relation.

$$R = \frac{1 \pm \sqrt{1 - e^{(-\alpha d)} + e^{(\alpha d)}}}{1 + e^{(-\alpha d)}}$$

The relation between linear refractive index (n) and reflectance (R) is given by

$$n = \frac{(R+1) \pm \sqrt{(3R^2+10R-3)}}{2(R-1)}$$

The evaluated values of reflectance and refractive index are given as a function of wavelength in the figures 3 and 4. From the results, it is confirmed that the samples have low absorption, low refractive index and low reflectance. When L-alanine crystals are added with barium chloride as the dopant, it seems that the optical parameters like reflectance and refractive index decrease as the doping concentration increases and it makes the samples that

are the prominent materials for antireflection coating in solar thermal devices and nonlinear optical applications.

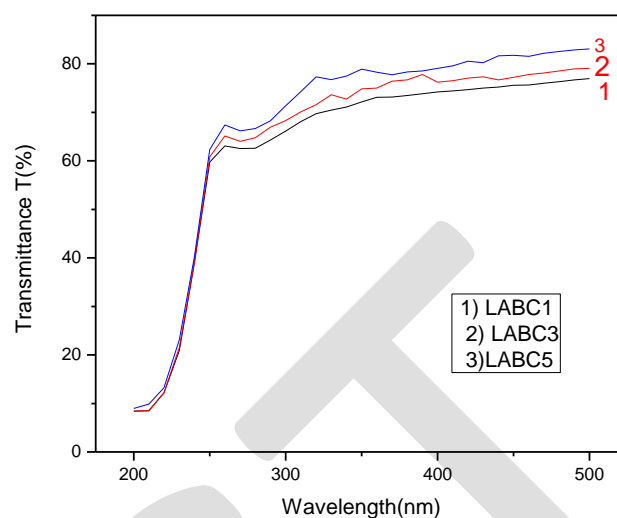


Fig.2: Optical transmission spectra of barium chloride doped L-alanine crystals

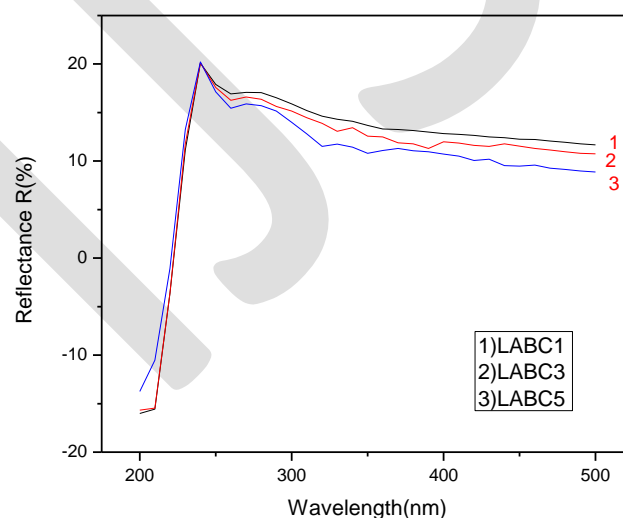


Fig.3: Variations of reflectance with wavelength for barium chloride doped L-alanine samples

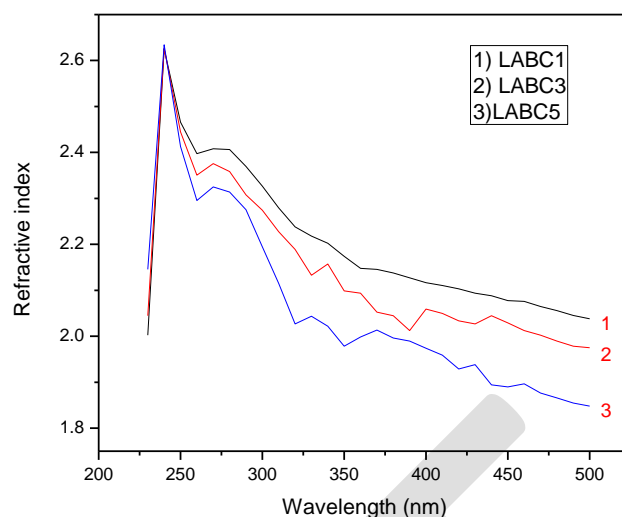


Fig.4: Variations of refractive index with wavelength for barium chloride doped L-alanine samples

3.3 Nonlinear optical analysis

The nonlinear optical (NLO) activity of the samples was confirmed using the Kurtz-Perry powder technique [16]. In this technique the powdered sample with an average particle sizes range 125–150 micron is filled in a micro-capillary tube about 1.5 mm diameter. Q-switched Nd: YAG laser (1064 nm Quanta ray Series, USA) emitting a fundamental wavelength of 1064 nm was used. The emission of green radiation (532 nm) confirms the second harmonic generation (SHG) of samples. The input laser energy incident on the samples was 0.68 J. The relative SHG efficiency of undoped L-alanine, LABC1, LABC3 and LABC5 samples are observed to be 0.34, 0.88, 0.93 and 0.98 respectively and here it is to be mentioned that KDP sample was used as the reference sample.

3.4 Hardness test

The microhardness test for the samples was carried out by carrying out by using as microhardness tester by applying different low loads. The hardness of a solid is defined as its resistance to local plastic/permanent deformation and the simplest way to obtain it is to press

a hard indenter of known geometry and to divide the applied load (P) by the area (A) of the indentation produced, i.e. hardness = P/A . The hardness of a material is usually calculated from the measured value of indentation diagonal length (d) produced by an applied load. Vickers microhardness values were calculated by using the formula $H_v = 1.8544 P/d^2$ kg/mm^2 where P is the applied load in kg, d is the mean diagonal length of the indentation in mm and 1.8544 is a constant of a geometrical fraction for the diamond pyramid. The traces of Vickers hardness number with a load for the undoped and barium chloride doped L-alanine crystals are shown in the figure 5. For all the samples, hardness is observed to be increasing with the increase of load and this is due to reverse indentation size effect and this can be explained qualitatively on the basis of depth of penetration of the indenter. For small loads, only a few surface layers are penetrated by the indenter. The measured hardness is the characteristics of these layers and hardness increases with load. With increase in load, the overall effect is due to surface as well as inner layers of the sample. The results show that the hardness increases when L-alanine is doped with barium chloride. The presence of barium chloride in the lattice of L-alanine crystals may be strengthening the bonds and hence the microhardness increases as the doping concentration of barium chloride increases.

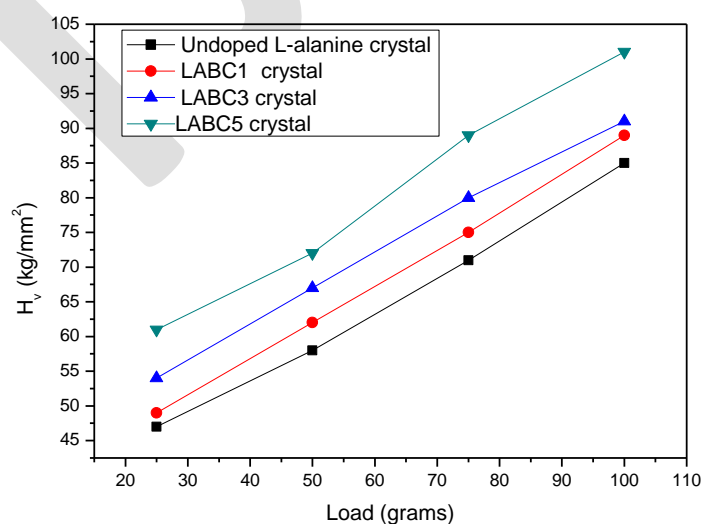


Fig.5: Variation of hardness values with the applied loads for the grown samples

3.5 Dielectric analysis

The dielectric constant and the dielectric loss factor are measured at different frequencies for various temperatures. The frequency dependence of the dielectric constant at different temperatures for LABC1 and LABC5 samples are shown in Figs. 6 and 7. It is observed that the dielectric constant has high values at lower frequencies and further decreases with increase in frequency and become independent at higher frequencies. The dielectric constant of the materials is due to the contribution of electronic, ionic, dipolar or orientation and a space charge polarization which is high rely upon on the frequencies [17]. The higher dielectric constant at lower frequencies is due to all active polarizations. The space charge polarization is generally active at lower frequencies and high temperatures. The variations of dielectric loss with frequency and temperature are presented in the figures 8 and 9. The low values of dielectric loss of the samples confirm the good quality of dielectric samples. The results show that values of dielectric constant and loss factor of the host L-alanine crystals are increased when they are doped with barium chloride.

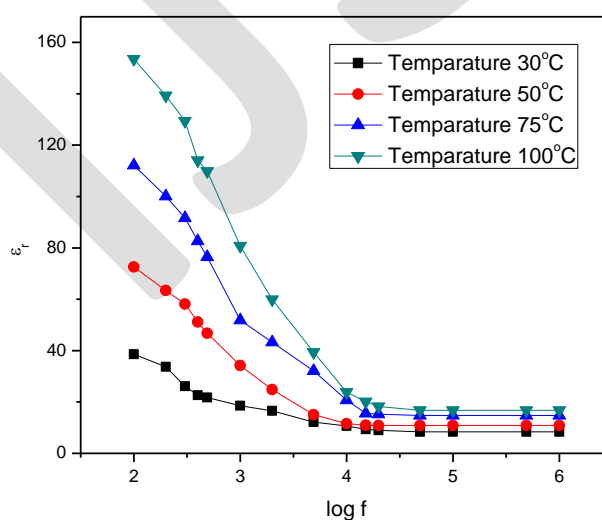


Fig.6: Variation of dielectric constant with frequency at different temperatures for LABC1 sample

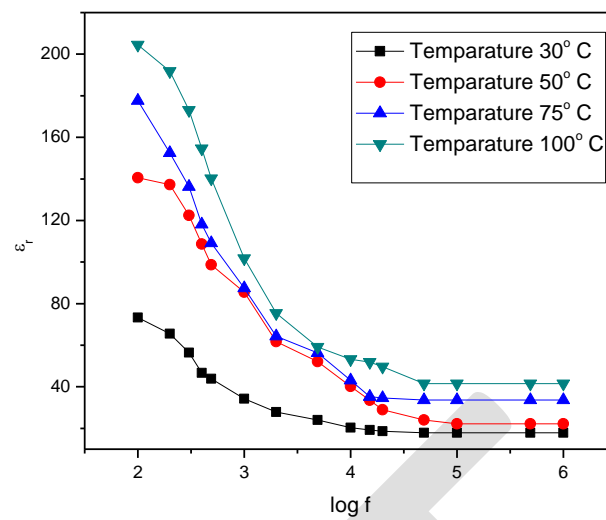


Fig.7: Variation of dielectric constant with frequency at different temperatures for LABC5 sample

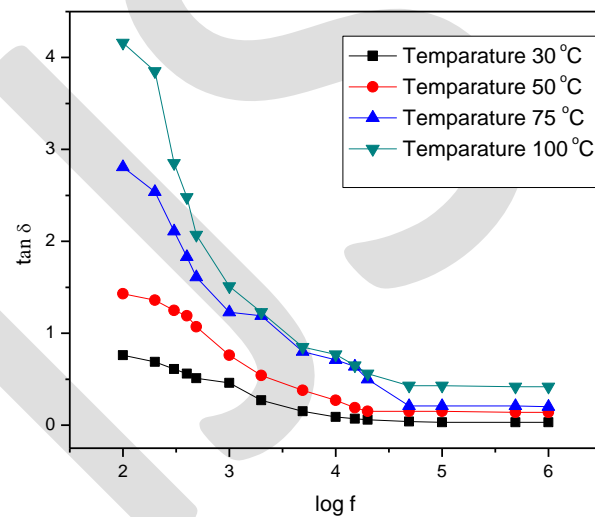


Fig.8: Variation of dielectric loss factor with frequency at different temperatures for LABC1 sample

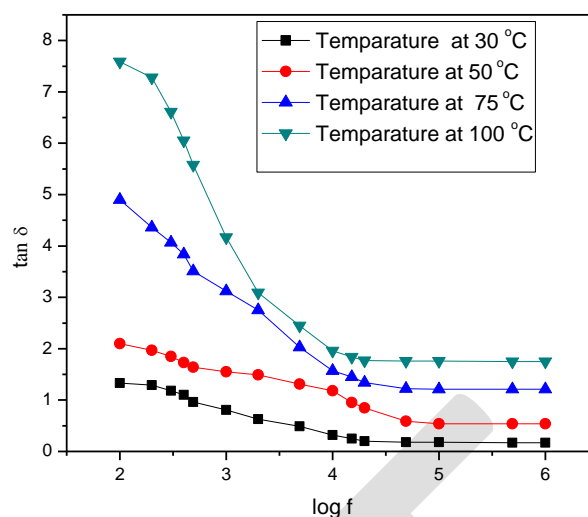


Fig.9: Variation of dielectric constant with frequency at different temperatures for LABC5 sample

4. Conclusions

Single crystals of undoped and barium chloride doped L-alanine have been grown from the aqueous solutions at room temperature. Solubility and nucleation studies were performed for the samples. The single crystal X-ray diffraction studies confirm that the grown crystals belong to the orthorhombic structure. The UV-vis-NIR spectra show a wide transparency window and this confirms that the samples are the potential candidates for NLO applications. The relative SHG conversion efficiency of the grown crystals was measured and it is found that the SHG efficiency of the barium chloride doped L-alanine samples are more than that of undoped L-alanine sample. The reflectance and refractive index values of the samples were determined from the data of optical transmittance spectra. The grown crystals of this work have stable dielectric constant values for the wide frequency range with low dielectric loss and it ascertains the dielectric behavior needed for opto-electronic devices. The hardness of L-alanine crystals is observed to be enhanced when it is doped with barium chloride.

Acknowledgement

The research supports given by IIT, Madras, STIC, Cochin University, Crescent Engineering College, Chennai and St. Joseph's College, Trichy are gratefully acknowledged.

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